Consumer and Corporate Affairs Canada
Consommation et Corporations Canada

(11) (A) No. 1147 908

(45) ISSUED 830614

(52) CLASS 8-57

(51) INT. CL.[3] C14C 1/00

(19) (CA) **CANADIAN PATENT** (12)

(54) SOAKING AND LIMING OF HIDES AND SKINS

(72) Lassen, Knud,
Germany (Federal Republic of)

(73) Granted to BASF Aktiengesellschaft
Germany (Federal Republic of)

(21) APPLICATION No. 362,658

(22) FILED 801017

(30) PRIORITY DATE Germany (Federal Republic of)
(P 29 42 964.9) 791024

No. OF CLAIMS 1 - NO DRAWING

Canada

DISTRIBUTED BY THE PATENT OFFICE, OTTAWA.
CCA-274 (11-82)

Abstract of the Disclosure: A process for soaking and liming hides and skins under conventional conditions, wherein the surfactants conventionally used are replaced by water-soluble salts of a carboxyl-containing polymer. This prevents foaming during soaking and liming and subsequent processes, and gives better leather.

Soaking and liming of hides and skins

The invention relates to a process for soaking and liming hides and skins under conventional conditions, wherein the surfactants conventionally used are replaced by water-soluble salts of a carboxyl-containing polymer. This prevents foaming during soaking and liming and subsequent processes, and gives better leather.

Soaking is the first step in the beamhouse, where all stages preceding actual tanning are carried out. Soaking is intended to remove adhering dirt, blood and any preservatives (especially sodium chloride) from the hide and to restore the hide to the swollen state which it possessed immediately after slaughtering.

Essentially, therefore, soaking comprises treating the hides and skins with water. The water should be very soft and (to suppress rotting) should also be cool. However, in the case of dried hides and skins, in particular, soaking with pure water would require a very long time and damage due to rotting would hardly be avoidable. It is therefore desirable to accelerate the soaking process and inhibit rotting. In the past alkalis were employed for this purpose, but nowadays a great variety of surfactants, some of which have a bactericidal action, are added for this purpose. However, the use of surfactants as a rule causes foaming, which is often a nuisance during soaking and subsequent processes, and can even effect tanning, not only because of frothing-over from open vessels, but

especially because of the problems of levelness during fatliquoring and dyeing and also during tanning. A further disadvantage of the use of surfactants is that the liming sludge hardens in the settling tanks. Finally, it is difficult to wash the surfactants completely out of the leather, and leather which contains a surfactant remains water-absorbent.

The next step in the production of leather, after soaking, is liming. It serves primarily to loosen the hair (hair-saving liming process) or destroy (pulp) the hair, chemically or enzymatically, and at the same time also to some extent opens up the skin, thereby preparing it for tanning. The commonest liming chemicals are lime and sulfide. More modern processes employ a mercaptan instead of an inorganic sulfide, and the lime can also advantageously be replaced, namely by sodium hydroxide solution in combination with sodium sulfate. Surfactants are also used as auxiliaries for accelerating the liming process and achieving a more even liming effect, but have the disadvantage of foaming, as already mentioned above. The use of sugar or molasses as liming auxiliaries is of less importance, for economic reasons.

It is an object of the present invention to provide an economical process for soaking and liming, having the advantageous effect of the surfactants hitherto used (namely an accelerating and leveling effect) without their disadvantages (ie. without the problem of foaming).

We have found that this object is achieved, according to the invention, by a soaking and liming process as set out in the claim. The amount of water-soluble salt of carboxyl-containing polymer to be employed is, for hides, from 0.2 to 2, preferably from 0.3 to 1, per cent by weight, based on the salted weight or soaked weight (or twice this percentage, if based on dry weight), and, for fur skins, from 0.2 to 2, preferably from 0.5 to 1, g/liter of liquor.

The advantages achieved on soaking are that the problems encountered when adding surfactants, as described above, are avoided. Furthermore, the novel auxiliary not only increases the rate of soaking, as compared to that achieved without a surfactant, but also gives cleaner hides, since the polycarboxylic acids have a fat-dispersing action. Furthermore, the hides treated by the novel process are more suitable for subsequent liming.

The advantages achieved during liming are that the problems resulting from added surfactant, as described above, are avoided. Furthermore, the novel additive causes the liming process to proceed more rapidly than when liming without a surfactant; the conventional amount of lime can be reduced by up to 50%, hence producing less pollution of the effluent; the liming effect is more even, since the solubility of the lime is increased, so that the lime penetrates the hide before the latter has become completely plump; creasing (drawn grain) barely occurs; the grain is

substantially cleaner; pigments, hair roots, sebaceous glands and residual fat are substantially removed. Because of being cleaner, the leather can also be dyed in more brilliant hues. A further advantage is that on subsequent tanning the chrome exhaustion is improved compared to what is conventionally achieved.

The conventional soaking conditions are a liquor length of from 70 to 400%, based on salted weight (if based on dry weight, the values are twice as great); the chemicals used are alkalis to bring the pH to 7-11, and/or surfactants in amounts of up to 2%, with or without bactericides, the amount of which depends on their effectiveness and on the desired effect; the temperature should be from 12 to 32°C, preferably from 20 to 25°C, and soaking requires from 5 to 48 hours.

The conventional chemical liming conditions are: a liquor length of from 50 to 400%, based on salted weight or soaked weight (these two roughly correspond); conventional liming chemicals, as already mentioned, the lime being used in excess (2 - 6% of the salted weight), ie. in larger amount than dissolves, so that there is always a saturated solution present, the inorganic sulfide being used in an amount of the order of 0.5 - 4%, based on salted weight, and the mercaptan in an amount of from 0.5 to 5%, depending onthe desired degree of pulping.

As regards the use of sodium hydroxide and sodium sulfate, with or without from 2 to 20 g/liter of substances which have a hydrotropic effect on albumen (for

a definition, cf. H. Römpp, Chemielexikon, 6th edition, Franck'sche Verlagshandlung Stuttgart, 1966, page 2,838), ie., in the main, water-soluble salts of organic acids, especially of sulfonic acids, carboxylic acids, hydroxysulfonic acids or sulfocarboxylic acids, and more particularly of 4-sulfophthalic acid, instead of lime and sulfide, reference may be made to German Patent 2,714,814. In enzymatic liming, surfactants, with or without bactericides, are employed in addition to the enzyme; the temperature should be about 37°C and the liquor length from 50 to 400%, based on salted weight.

The carboxyl-containing polymer or salt thereof may, according to the invention, be employed either only during soaking or only during liming or, preferably, during both. The K value of the fully neutralized salt (ie. the salt obtained with 1 mole of NaOH or NH_4OH per mole of carboxyl groups, the pH of a 1% strength solution of such a salt being from 8 to 9), determined by the method of H. Fikentscher, Cellulosechemie 13 (1932), 58 - 64 and 71 - 74, should, in 5% strength sodium chloride solution at 20°C, be from 10 to 150, preferably from 30 to 100.

For the purposes of the invention, carboxyl-containing polymers are especially the homopolymers of acrylic acid or methacrylic acid, and the copolymers of acrylic acid, methacrylic acid, maleic acid or maleic anhydride

with other ethylenically unsaturated compounds, provided that their sodium salts and ammonium salts are soluble at the stated use concentrations and under the use conditions (ie., for soaking of salted hides and skins, at relatively high concentrations of salt in the soaking liquor; for liming, in a saturated calcium hydroxide solution). The copolymers may contain up to 80, preferably up to 60, per cent by weight of ethylenically unsaturated compounds which do not contain a carboxyl group and are copolymerizable with acrylic acid, methacrylic acid or maleic anhydride, eg. acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, acrylic acid esters, methacrylic acid esters, ethylene, isobutene, styrene and vinyl isobutyl ether. Of course, with a view to the neutralized polymers being water-soluble, higher proportions of hydrophilic comonomers than of hydrophobic comonomers can be used. The particularly preferred polymers contain from 0 to 50% by weight of the carboxyl-free comonomers; they may also contain a plurality of comonomers as copolymerized units - for example, copolymers of acrylic acid, acrylonitrile and acrylamide may be used. The appropriate copolymers are known and are obtained by polymerizing acrylic acid or methacrylic acid or copolymerizing these, or maleic anhydride, with suitable comonomers. It is important that the polymers should be water-soluble at a neutral pH (when they are partially

neutralized) or at least at a slightly alkaline pH (when they are fully neutralized), ie. at a pH of from 7 to 9.

In principle, not only the sodium salts and ammonium salts, but other water-soluble salts of the stated polymers could be used, but these are ruled out for industrial purposes, on economic grounds.

The salts are obtained by polymerizing the sodium salts or ammonium salts of acrylic acid or methacrylic acid, or copolymerizing them with suitable comonomers, or by neutralizing the polymers of the stated acids with ammonia or preferably with sodium hydroxide solution, or by copolymerizing maleic anhydride with comonomers, eg. styrene, ethylene, 1-olefins, such as isobutene, or vinyl isobutyl ether, preferably in a molar ratio of 1 : 1, and then hydrolyzing the anhydride groups with an equivalent amount of sodium hydroxide solution.

In the Examples, liquor lengths and percentages are based either on salted weight or soaked weight, or on dry weight, of the hides and skins, which

ever condition of the hides and skins is referred to in the introductory sentence of the particular Example.

EXAMPLE 1

Soaking of salted raw hides:

200 % of water at 28°C
0.5% of sodium polyacrylate, K value 40
0.3% of calcined sodium carbonate
6 hours

The soaking time is about 30% shorter than when using the same formulation without the additive according to the invention.

EXAMPLE 2

Soaking of air-dried raw hides:

400 % of water at 28°C
1 % of the sodium salt of a copolymer of 60 parts by weight of acrylonitrile and 40 parts by weight of acrylic acid; K value 80
0.5% of calcined sodium carbonate
10 hours, drain off the liquor.

Resoaking:

300 % of water at 28°C
0.5% of the above copolymer salt
0.2% of calcined sodium carbonate
8 hours

The soaking is 30-40% faster than when using the same formulation without the additive according to the invention; the water pick-up of the soaked hide is

substantially greater; fleshing after soaking is facilitated.

EXAMPLE 3

Soaking of salted raw fur skins:

500 % of water at 28°C

0.5 g/l of the ammonium salt of a copolymer of 35 parts by weight of acrylonitrile and 65 parts by weight of acrylic acid, K value 125

8 hours in a paddle vat, running 10 minutes per hour.

Soaking is about 30% faster; fleshing after soaking is facilitated; the flesh side and, in the case of light-colored furs, also the hair, is substantially lighter than after soaking without the additive according to the invention.

EXAMPLE 4

Soaking of air-dried raw furs:

1,000 % of water at 28°C

1 g/l of the sodium salt of a polyacrylic acid of K value 40

15 hours in a paddle vat, running for 10 minutes per hour.

Soaking is 50% faster than without the additive according to the invention; fleshing after soaking is substantially facilitated, due to the greater water pick-up; the flesh side and, where relevant, the hair are once again substantially lighter.

EXAMPLE 5

Liming of salted raw hides:

150 % of water at 28°C
0.3% of the ammonium salt of a polyacrylic acid of K value 40
0.5% of sodium hydrosulfide (NaHS)
2 % of 60% strength sodium sulfide
2.5% of slaked lime
18 hours

The liming chemicals penetrate the pelts substantially more rapidly; the chemicals are more uniformly distributed through the cross-section of the hide, giving smoother pelts (less drawn grain); the color of the pelts is lighter, due to the easier removal of the scud (hair pigments); mechanical processing on the fleshing machine is easier; due to the improved solubility of the lime, lime blast after rinsing is less pronounced.

EXAMPLE 6

Liming of dried goatskins:

100 % of water at 28°C
0.5% of the sodium salt of a copolymer of styrene and maleic anhydride (molar ratio 1 : 1), of K value 40
3 % of 60% strength sodium sulfide
3 % of slaked lime
18 hours

Resoaking:

200 % of water at 28°C

2 % of slaked lime

0.2% of the above copolymer salt

12 hours

The opening-up action of the soak is faster, the pelts are smoother and cleaner, the color is lighter, the mechanical working of the pelts (fleshing and scudding) is easier and on rinsing with hard water, lime blast is avoided.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

A process for soaking and liming of hides and skins by treating the dried or salted hides and skins with from 70 to 400%, based on salted weight, of a soaking or liming liquor which contains no surfactants but for soaking may contain alkalis and bactericides, for chemical liming contains, based on salted weight, from 2 to 6% of lime and from 0.5 to 4% of an inorganic sulfide or from 0.5 to 5% of a mercaptan or, in place of lime and sulfide or mercaptan, contains from 15 to 150 g/liter of sodium hydroxide and from 50 to 200 g/liter of sodium sulfate and/or of the sodium salt of a dicarboxylic acid of 3 to 6 carbon atoms, and may or may not contain from 2 to 20 g/liter of substances having a hydrotropic action on albumen, and in the case of enzymatic liming contains the enzyme with or without bactericides, for from 5 to 48 hours at a pH of from 7 to 11 and at from 12 to 32°C, wherein the liquor contains, in the case of hides, from 0.2 to 2% by weight, and in the case of fur skins, from 0.2 to 2 g per liter of liquor, of a water-soluble sodium salt or ammonium salt of a polymer which contains, as polymerized units, not less than 20 mole per cent of a monomer possessing one or more carboxyl groups, and which has a Fikentscher K value of from 10 to 150.